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(54) Title: PROCESS FOR STAINLESS STEEL PICKLING																	
(57) Abstract																	
<p>This invention is related to a process for pickling metals, especially rust resistant steel materials, preferably for removing mill scale and other oxide layers, which is characterized in that the metal is brought into contact with a pickling agent comprising, in aqueous solution, in per cent by weight: H<sub>2</sub>SO<sub>4</sub> 5-35, H<sub>3</sub>PO<sub>4</sub> 5-35, fluoride ion (HF) at least 0.1, Fe<sup>3+</sup> at least 0.4, optionally other in pickling agents commonly used additives, such as surface active agents H<sub>2</sub>O up to the rest (up to 100 %) and additionally optionally thickening agents and fillers. The invention is also related to a pickling agent for said process and a concentrate for preparing said pickling agent.</p>																	
<p>The graph plots 'Pickling power / Pickling speed' on the y-axis against '% by weight of Fe<sup>3+</sup> in solution' on the x-axis. The x-axis has markers at 1, 2, and 3. The curve starts at point A (approx. 0.2% Fe<sup>3+</sup>), rises steeply to a peak at point B (approx. 0.8% Fe<sup>3+</sup>), and then gradually declines through point C (approx. 2.5% Fe<sup>3+</sup>). Vertical dashed lines are drawn at approximately 0.5% and 1.2% Fe<sup>3+</sup>.</p> <table border="1"><caption>Approximate data points from the graph</caption><thead><tr><th>% by weight of Fe<sup>3+</sup> in solution</th><th>Pickling power / Pickling speed (relative)</th></tr></thead><tbody><tr><td>0.2 (Point A)</td><td>Low</td></tr><tr><td>0.5</td><td>Low</td></tr><tr><td>0.8 (Point B)</td><td>High (Peak)</td></tr><tr><td>1.2</td><td>High</td></tr><tr><td>2.5 (Point C)</td><td>Medium</td></tr><tr><td>3.0</td><td>Medium-Low</td></tr></tbody></table>				% by weight of Fe <sup>3+</sup> in solution	Pickling power / Pickling speed (relative)	0.2 (Point A)	Low	0.5	Low	0.8 (Point B)	High (Peak)	1.2	High	2.5 (Point C)	Medium	3.0	Medium-Low
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0.8 (Point B)	High (Peak)																
1.2	High																
2.5 (Point C)	Medium																
3.0	Medium-Low																

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## Process for stainless steel pickling

This invention is related to a process for pickling metals, especially rust resistant (stainless) steel materials, especially for removing mill scale and other oxide layers. Said process is characterized in that the metal is brought into contact with a pickling material comprising, in aqueous solution, in per cent by weight:

$\text{H}_2\text{SO}_4$	5 - 35
$\text{H}_3\text{PO}_4$	5 - 35
HF	at least 0.1
$\text{Fe}^{3+}$	at least 0.4

optionally other in pickling agents commonly used additives, such as surface active agents

$\text{H}_2\text{O}$	up to the rest (up to 100%)
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and additionally optionally thickening agents and fillers.

Pickling of metals of the type stainless steels and similar is a well-known type of surface treatment which is used for improving the surface of said materials and is disclosed in a number of publications, among these patents, to which publications reference is made as regards the common knowledge of those skilled in the art in the field in question.

Stainless steels and similar materials, for which the process according to this invention is especially suited, are also disclosed in a number of publications, and reference is made in this respect e.g. to the publication "Stahlschlüssel", the paragraph with the title "Stainless Steels", "Metals Handbook" issued by "American Society For Metals", especially the

part "Corrosion-Resistant Materials" and the SS norms for stainless steels. All these materials can normally be treated by the process according to this invention, especially chromium-nickel and chromium-nickel-molybdenum alloyed stainless (rust resistant) steels. These steels can be of e.g. ferritic, austenitic, martensitic and duplex type. Examples of such steels are e.g. SS 2343 and 2333. These steels contain usually chromium in a content of from 10 up to 35% by weight or more and usually also nickel in a content of from 3 up to 25% by weight or more and optionally molybdenum in contents of usually up to 10% by weight. Also other types of alloys, such as high temperature alloys, refractory alloys (super alloys) based on chromium and/or nickel, and also other metal elements and alloys of these can be treated in accordance with this invention.

The process according to this invention is used on the first hand for treating metals with an oxide layer on the surface, such as oxide layers remaining after hot working or casting or heat treatment, e.g. mill scales or oxide layers remaining after welding, e.g. gas welding, arc welding, e.g. with tubular electrodes or pin electrodes, MMA welding, MIG welding and TIG welding.

Essential constituents of the pickling agent according to this invention are sulphuric acid and phosphoric acid.

The content of sulphuric acid,  $H_2SO_4$ , calculated as non-aqueous substance, in the ready-for-use solution is, in per cent by weight of the solution, at least 5, suitably at least 7, at least 10 or at least 12, and preferably at most 35, at most 30, at most 22, at most 18, usually suitably about 15.

The content of phosphoric acid,  $H_3PO_4$ , calculated as non-aqueous substance, in the ready-for-use solution is, in per cent by weight of the solution, at least 5, preferably at

least 7, at least 10 or at least 12, and preferably at most 35, at most 30, usually suitably at most 22, at most 18 or about 15.

The combined content of sulphuric acid and phosphoric acid is, in per cent by weight of the solution, preferably at least 10, at least 14, at least 20 or at least 24, and usually at most 70, at most 50, at most 44 or at most 35 or about 30.

A frequently preferred range of sulphuric acid and phosphoric acid is from 7 up to 22% by weight of each, e.g. about 15% by weight of each, e.g. with variations of up to 2 or 4% of each acid from said approximate value, calculated as non-aqueous substances and in per cent by weight of the solution.

Further constituents are preferably fluoride ion (hydrofluoric acid) in a quantity of, calculated in per cent by weight of the solution, at least 0.1 and preferably, with regard to the poisonousness, up to at most 1 or at most 0.9, e.g. about 0.8, but also higher contents can be used, e.g. up to at most 10 or at most 5 or also at most 2.

The pickling agent comprises, furthermore, ferric ion,  $\text{Fe}^{3+}$ , which is believed to act as an oxidizing agent, in an active content, calculated in per cent by weight of the solution, of above 0.1, preferably at least 0.4% by weight, or above, e.g. at least 0.6 or preferably at least 1 or at least 1.2. The upper content limit is usually at 10 or 5 or optionally 2. Together with a content of  $\text{Fe}^{3+}$  within the mentioned limits also other oxidizing agents may optionally be used, such as other elements which are present in various oxidation states (valencies) wherein said other oxidizing agents preferably have an effect similar to that of  $\text{Fe}^{3+}$  and preferably are used in quantities which give an effect corresponding to that of the stated content ranges of  $\text{Fe}^{3+}$ , or give a redox

potential which corresponds to that of  $\text{Fe}^{3+}$  in the stated content ranges. The content of ferric ion and/or ferrous ion and/or the redox potential can be monitored, and when required restored to the desired values (content value and/or redox potential), e.g. with supplementing additions and reoxidizing of ferrous ion to ferric ion. The reoxidation can be achieved e.g. with air, oxygen gas, ozone, peroxy compounds, such as hydroperoxide, ammonium persulphate or other persulphates, with additions to the bath or to a branched-off flow of the bath. The additives can be controlled so that the preferred maximum contents are not exceeded. In some cases it seems that e.g. the content ratio of ferric ion/ferrous ion can be maintained at a value corresponding in the solution to an oxygen partial pressure of at least 0.01 atm, at least 0.1 atm, at least 0.5 atm, at least 1 atm or at least 10 atm, and/or a content ratio of e.g. at least 0.1, at least 1, at least 5, at least 10 or at least 50. The metal content in the bath can continuously or intermittently be corrected by extracting, adsorbing or precipitating metals, e.g. chromium, nickel, iron and others, e.g. with ion exchangers or hydroxides, e.g. calcium hydroxide, e.g. to a pH value of at least 9 or at least 11-12.

Preferably the pickling agent is free from or essentially free from such other oxidizing agents, especially such as per(oxy) compounds, e.g. hydroperoxide, nitro compounds, e.g. nitro substituted aromatic compounds, e.g. nitrobenzene sulphonate, or contains such in a restricted quantity, e.g. less than 1%, less than 0.5% or less than 0.1%, based on the weight of the solution.

Preferably the pickling agent is free from or comprises at most a low content of nitrate ion or nitric acid, e.g. at most 2 or at most 1, usually at most 0.5 or at most 0.1% by weight thereof or at most a quantity which is introduced as impurity or is dragged e.g. from a previous bath in a treat-

ment line.

Preferably the pickling agent is free from chlorine compounds, especially such which may cause corrosion, especially pitting corrosion, such as chloride ions, or contains such in a quantity which does not cause corrosion, e.g. pitting corrosion.

The rest of the pickling solution consists preferably of water up to 100% by weight besides additives which are commonly used in pickling agents. One such additive is wetting agents (surface active agents) which are suitably present in a quantity of at least 0.1% by weight and usually up to 1% by weight. Usually non-ionic wetting agents are used, e.g. of the polyalkoxy alkylphenol type, such as polyethoxy and/or propoxy nonylphenol type.

The treatment temperature or bath temperature can be maintained from room or ambient temperature, e.g. 15 to 25°C, up to the boiling point of the bath or preferably up to about 80, up to about 60 or up to about 40°C. The treatment time is the period of time which with the temperature and the materials used gives cleaning, such as removal of mill scale and other oxide layers. Commonly used times at 15-25°C are from 30 to 150 minutes, frequently 40 to 90 minutes.

The pickling agent according to this invention can also, in addition to the constituents mentioned above, contain thickening agents and/or fillers, especially in such a quantity that the pickling agent can be applied on surfaces in a quantity which is effective for pickling, especially as a pickling paste. A suitable thickening agent is barium sulphate or other previously used thickening agents, such as sulphates, phosphates, silicates or oxides, preferably in quantities up to 200% or up to 150% of the weight or volume of the pickling agent solution disclosed herein.

This invention comprises also a concentrate for preparing the pickling solution or pickling paste according to the invention. Said concentrate suitably exhibits the content ratios of the constituents, besides water, of the desired pickling solution according to the invention, which by the addition of a further quantity of water gives the desired composition of the solution of the bath and the paste resp. The content of water in the concentrate may be e.g. at most 60%, at most 50%, at most 35% or at most 25%.

When using the process according to this invention for treating metals, such as rust resistant or slow rusting steels and other alloys of the types which are disclosed or exemplified herein, it is possible to achieve an extremely clean surface with good surface smoothness and little attack at the grain boundaries, and with a bright and/or a satin appearance. This can be achieved with a pickling agent with a low content of especially poisonous, poison releasing or difficult to handle constituents, such as hydrofluoric acid and nitric acid-nitric ion in higher contents, and with the use of an easily handled and low cost oxidizing agent consisting of ferric ion.

In the following a number of examples of the use of the process according to this invention for pickling of chromium-nickel containing alloys, such as stainless steels, are disclosed. The used pickling bath exhibited the following composition:

	% by weight
Sulphuric acid, $\text{H}_2\text{SO}_4$ (405 kg, 37%)	15
Phosphoric acid, $\text{H}_3\text{PO}_4$ (176 kg, 85%)	15
Ferric ion, $\text{Fe}^{3+}$ ( $\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , 60 kg)	1.2
Fluoride ion, $\text{F}^-$ (HF, 40%, 20 kg)	0.8
Surface active agent (APSA-80, 4 kg)	0.4
Water	up to 100



The conditions and the results of the tests are obvious from the following table. The results are related to the average results from 12 pickling experiments.

Treatment with pickling bath, welded material

<u>Steel type</u>	<u>Welding method</u>	<u>Electrode</u>	<u>Time min</u>	<u>Temp. °C</u>
SS 2343	MMA	19,12,3 LR	40-45	15-18
"	MIG	19,12,3 LSi	50-60	"
SS 2333		tube electrode	40-50	"
"		coated rod	40-50	"

Treatment with pickling paste (450 g of the pickling solution disclosed above + 550 g of barium sulphate), welded material

<u>Steel type</u>	<u>Welding method</u>	<u>Electrode</u>	<u>Time min</u>	<u>Temp. °C</u>
SS 2343	MMA	19,12,3 LR	75-90	15-18
"	MIG	19,12,3 LSi	90-120	"
SS 2333		tube electrode	70-80	"
"		coated rod	70-80	"

Further experiments were performed with the same type of pickling solution on cold rolled annealed tubes with the compositions stated below and at a temperature of 40°C:

Steel designation		Chemical analysis			
<u>Sandvik</u>	<u>Norm</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Others</u>
3R65	SS 2348	17	11.5	2.1	
3R60	SS 2353	17.5	13	2.6	
8R30	SS 2337	17.5	10		Ti
2R60	SS 2353	17.5	14	2.6	
3R64	SS 2367	18.5	14.5	3.1	
8R11	16031	18	8		
3R12	SS 2352	18.5	10		
10R19	SS 2368	21	11	<3	N, Ce
2RK25	SS 2562	20	25	4.5	Cu 1.5
San31HT	Alloy 800	21	31		Al/Ti = 0.5
BR70	SS 2350	17	13	2.1	Ti
3RD60	SS 2376	18.5	4.9	2.7	N
	SS 2378	20	18	6.1	Cu 0.7, N
2RE10	SS 3518	24.5	20.5		
	SS 2328	25	7	4	N
San28Cu	SS 2584	27	31	3.5	Cu 1.0

In all experiments very good cleaning and removal of mill scale and other oxide layers remaining from working, heat treatment and welding were achieved with a fine surface appearance with good gloss. The results were at least equal to or superior to the results of a simultaneous comparative pickling with a conventional nitric acid-hydrofluoric acid pickling bath containing 16% by weight of nitric acid and 4% by weight of hydrofluoric acid.

Furthermore, the enclosed figure shows the result of pickling experiments performed on stainless steels with the pickling paste disclosed above, and the influence of the content of  $\text{Fe}^{3+}$  on the result of the pickling experiments.

"The pickling power/pickling speed" disclosed along the vertical axis on the figure is a weighted total of the cleanliness and appearance of the pickled surface and the pickling

speed. Within the content area denoted "A" a low pickling effect was achieved, within the area denoted "B" optimum pickling effect was achieved with short pickling times and clean and bright weld surfaces, and within the area "C" good pickling effect was achieved with clean and bright weld surfaces, but with a pickling time which increased to some extent with increasing ferric ion content.

CLAIMS

1. A process for pickling metals, especially rust resistant steel materials, preferably for removing mill scale and other oxide layers, characterized in that the metal is brought into contact with a pickling agent containing, in aqueous solution, in per cent by weight:

$H_2SO_4$	5 - 35
$H_3PO_4$	5 - 35
HF	at least 0.1
$Fe^{3+}$	at least 0.4

optionally other in pickling agents commonly used additives, such as surface active agents

$H_2O$	up to the rest (up to 100%)
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and additionally optionally thickening agents and fillers.

2. A process according to claim 1, characterized in that the metal is brought into contact with a pickling agent which comprises, in per cent by weight:

HF	preferably at most 1
$Fe^{3+}$	at least 0.6, preferably at least 1 and at most 10, preferably at most 5

optionally surface active agent, preferably at least 0.1 and especially at most 2.

3. A process according to claim 1 or 2, characterized in that the metal is brought into contact with a pasty pickling agent comprising fillers and/or thickening agents, preferably in a quantity of up to 200% of the weight of the solution.

4. A process according to any of the preceding claims, characterized in that the metal is brought into contact with a pickling agent which as thickening agents

comprises a barium compound, especially barium sulphate.

5. A process according to any of the preceding claims, characterized in that the pickling agent as a surface active agent comprises a nonionic surface active agent, especially of the polyalkoxy-nonylphenol type, e.g. APSA-80 or a similar product.

6. A process according to any of the preceding claims, characterized in that the pickling solution comprises at most 1% of nitrate ion (or  $\text{HNO}_3$ ), preferably at most 0.5 or at most 0.1% of nitrate ion and preferably is free from nitrate ions, optionally with the exception of impurity levels thereof, which are introduced e.g. with the bath components used or with the articles subjected to pickling.

7. A process according to any of the preceding claims, characterized in that one or more further oxidizing agents are used together with  $\text{Fe}^{3+}$ , with the exception of nitric acid or nitrate.

8. A pickling agent which is suited for carrying out the pickling process according to any of the preceding claims, characterized by comprising, in per cent by weight:

$\text{H}_2\text{SO}_4$	5 - 35
$\text{H}_3\text{PO}_4$	5 - 35
HF	at least 0.1, preferably at most 1
$\text{Fe}^{3+}$	at least 0.4, preferably at most 10

optionally in pickling agents commonly used additives, such as surface active agents

$\text{H}_2\text{O}$  up to the rest (up to 100%)

and additionally optionally thickening agents and fillers, the pickling agent preferably being free from nitrate ions or comprising nitrate ions in a content of at most 2, preferably at most 0.5 or at most 0.1% by weight.

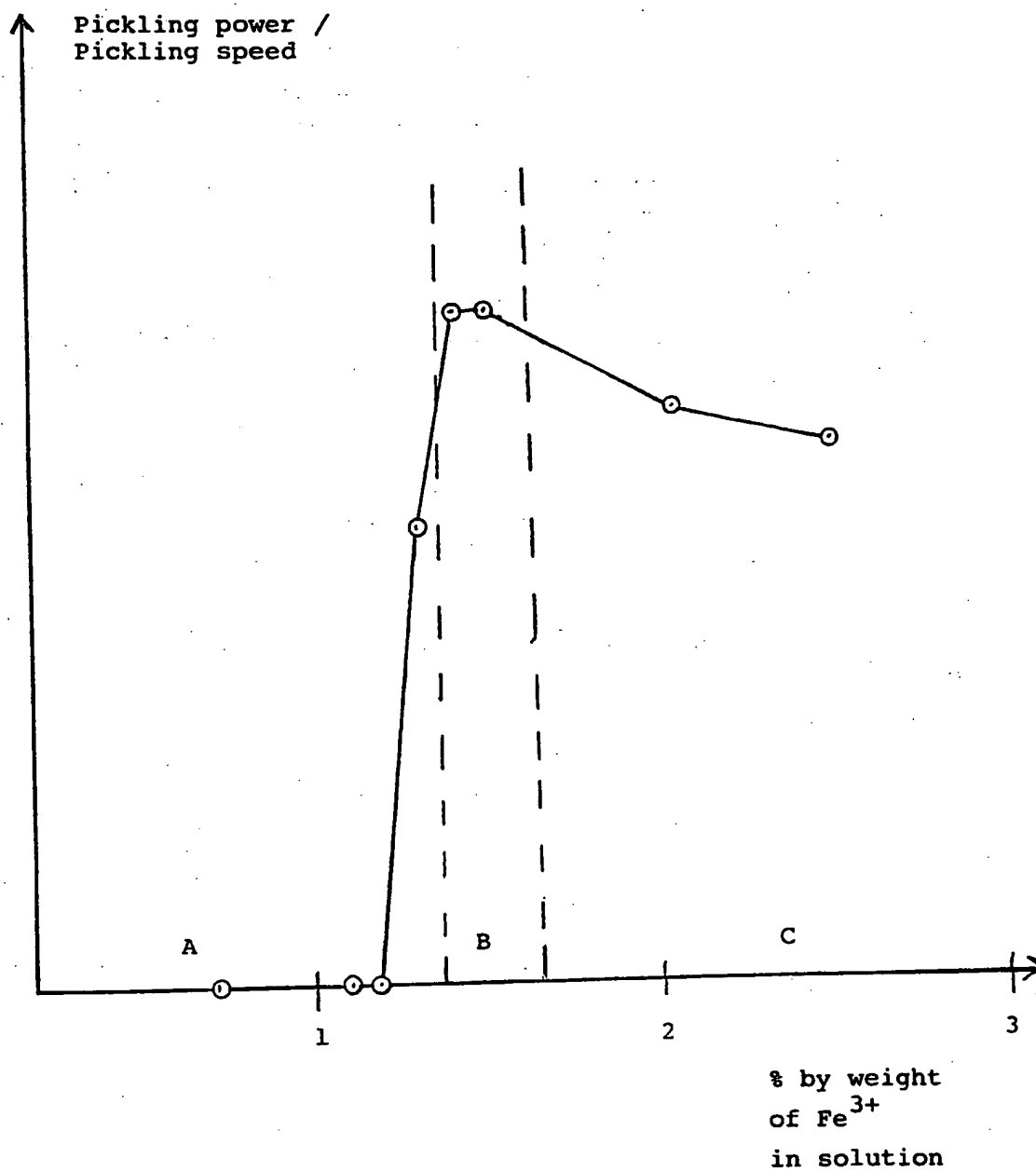
9. A pickling agent according to claim 8, characterized by comprising in solution, in percent by weight:

$H_2SO_4$	7 - 22
$H_3PO_4$	7 - 22
HF	less than 1
$Fe^{3+}$	at least 0.6

and in addition to this optionally thickening agents or fillers in a quantity of up to 200% by weight of the weight of the solution.

10. A concentrate for preparing a pickling material according to claim 8 or 9, characterized by comprising the pickling solution constituents concentrated to a water content of at most 50% by weight and preferably at most 25% by weight of the concentrate.

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 95/00748

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C23G 1/08 // C23G 1/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C23F, C23G, C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

ORBIT: WPAT, CLAIMS, JAPIO

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0582121 A1 (ITB S.R.L.), 9 February 1994 (09.02.94), claims 1,3,6, abstract	1-10
Y	US 3598741 A (SHOZO KANNO), 10 August 1971 (10.08.71), column 1, line 47 - line 48; column 3, line 46 - line 55; column 4, line 3 - line 8, column 4, line 39 - line 51, claims 1,9 and abstract	1-10
A	EP 0592892 A1 (ITB S.R.L.), 20 April 1994 (20.04.94), claim 1, abstract	1-10

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search

11 Sept 1995

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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/SE 95/00748

**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9105079 A1 (INTEROX CHEMICALS LIMITED), 18 April 1991 (18.04.91)  --	1-10
A	US 2923608 A (PAUL H. MARGULIES), 2 February 1960 (02.02.60), column 2, line 46 - line 49  -- -----	1-10

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

28/08/95

International application No.

PCT/SE 95/00748

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0582121	09/02/94	NONE	
US-A- 3598741	10/08/71	DE-A,B,B 1950560 GB-A- 1279834	23/04/70 28/06/72
EP-A1- 0592892	20/04/94	NONE	
WO-A1- 9105079	18/04/91	AT-T- 113670 DE-D,T- 69013896 EP-A,B- 0457859 SE-T3- 0457859 ES-T- 2066226 US-A- 5364549	15/11/94 09/03/95 27/11/91  01/03/95 15/11/94
US-A- 2923608	02/02/60	NONE	